

Section 8--Sigma Bonds and Bond Rotation

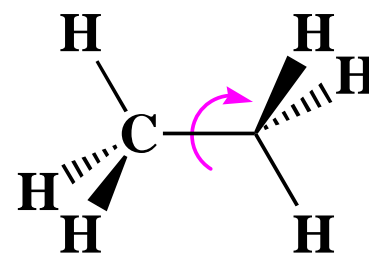
Sigma Bonds and Bond Rotation

Rotation is possible around single bonds (sigma bonds). The orientations of atoms and groups that result from rotation are called **conformations**.

Different conformations may have different energies. An analysis of the energy changes with rotation around a bond is called **conformational analysis**.

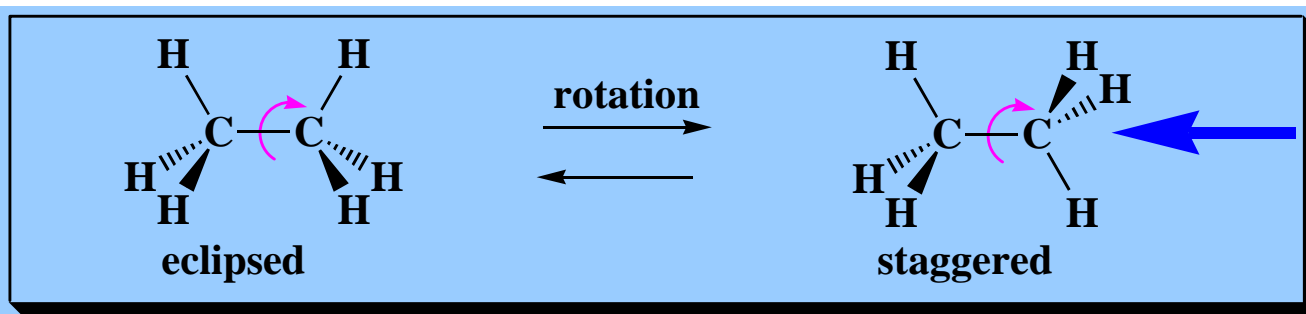
Conformational Analysis of Ethane: $\text{H}_3\text{C}-\text{CH}_3$

An **energy barrier** of close to 12.6 kJ/mol is observed during rotation around the C-C bond in ethane. This energy barrier is attributed to **torsional strain**.

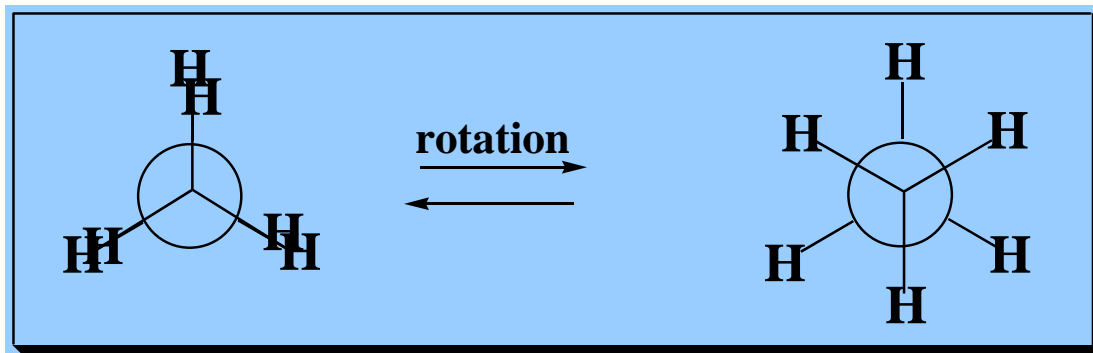


The Conformations of Ethane

An analysis of the rotation around the C-C bond in ethane shows there are **two extreme conformations**. These two conformations called **eclipsed** and **staggered** are shown below. These two conformations interconvert by simple rotation around the C-C bond.



The relative orientations of the hydrogens around the two carbons are easier to see in a **Newman projection formula**, wherein the structure is viewed along the carbon-carbon bond.



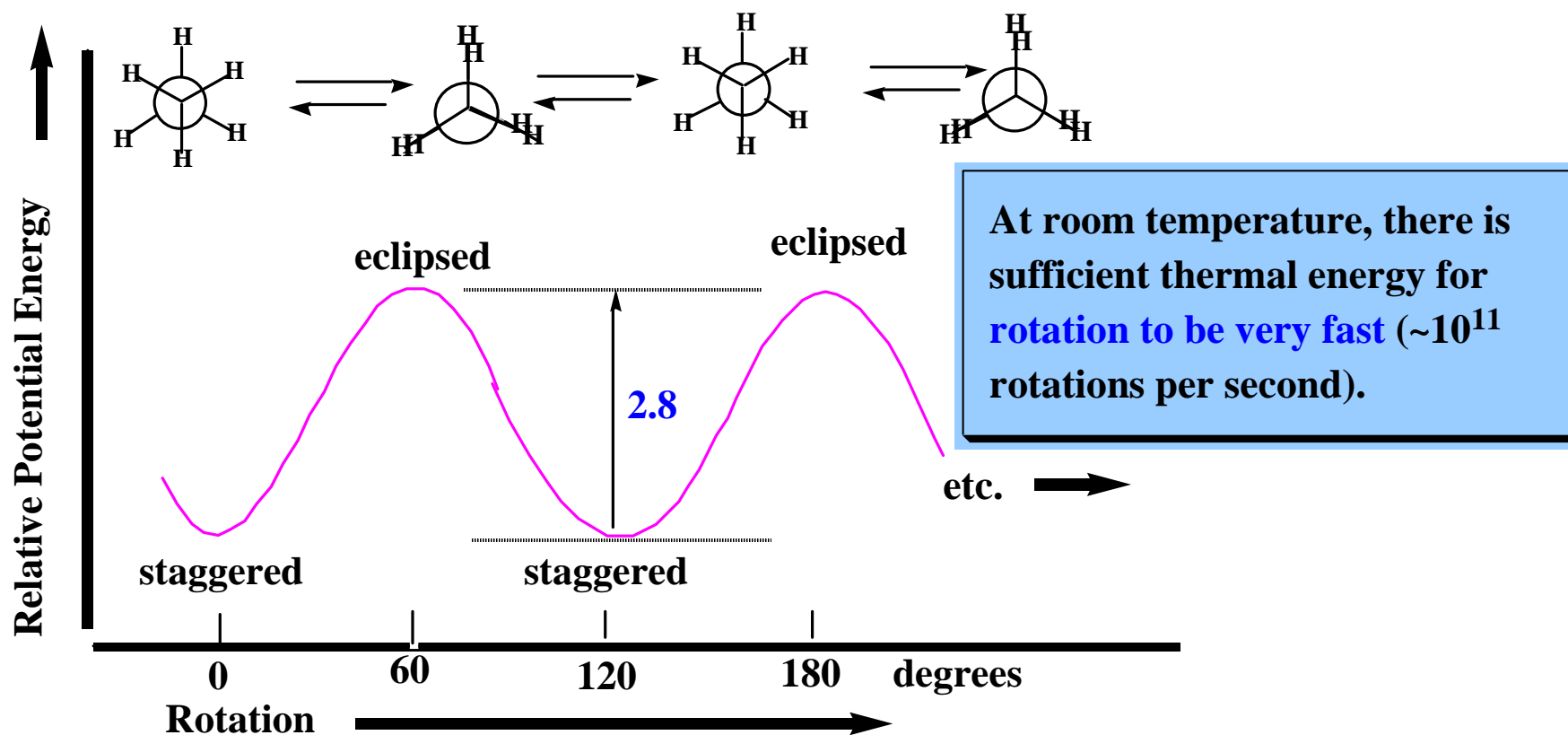
The **intersection of the three bonds** represents the orientation of the three H around the **front carbon**, and the **lines to the circle** represent the orientation of the three H around the **back carbon**.

Relative Energies of the Staggered and Eclipsed Conformations

The rotational barrier of **11.72 kJ/mol** is associated with the **eclipsed conformation** where the H on the two carbons are aligned. This energy barrier is called the **torsional barrier**, and the source of the increased energy, relative to the staggered conformation, is called **torsional strain**. The cause of the torsional strain in the eclipsed conformation of ethane is not simply nonbonding repulsive interactions between the H (steric strain).

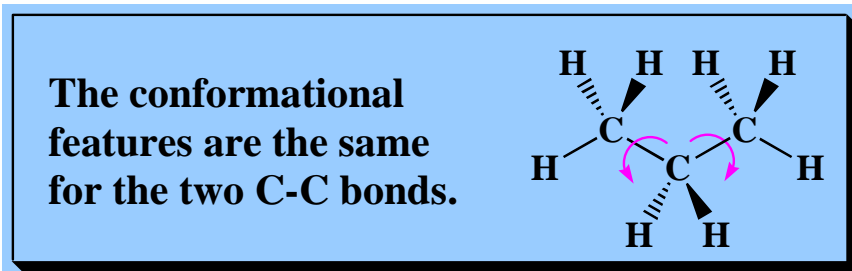
Conformational Energy Diagram for Ethane

The diagram below shows the change in potential energy in ethane with rotation around the C-C bond. In one complete rotation of 360° , **three equal barriers of 11.72 kJ/mol** are encountered.

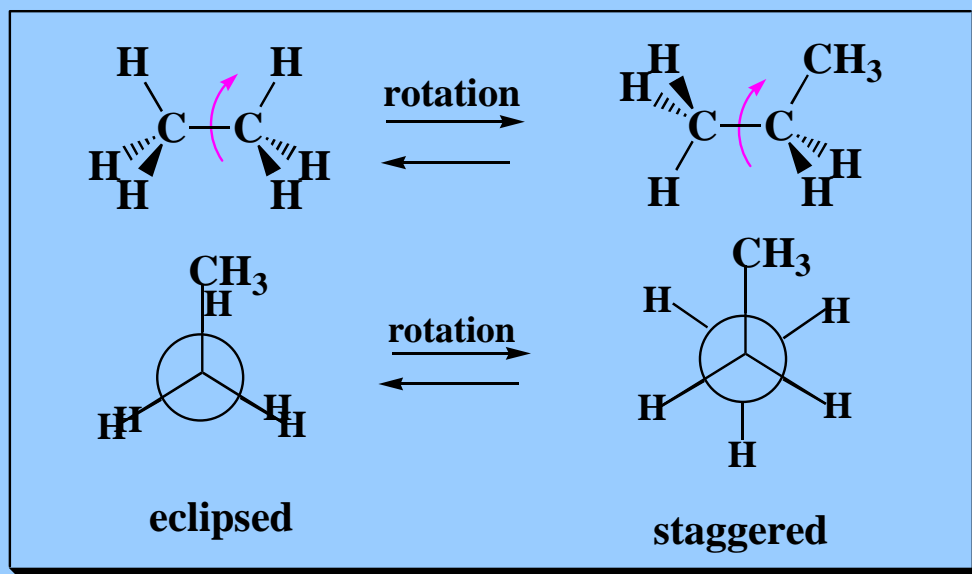


The Conformations in Propane: $\text{CH}_3\text{-CH}_2\text{-CH}_3$

There are two equivalent C-C bonds in propane:

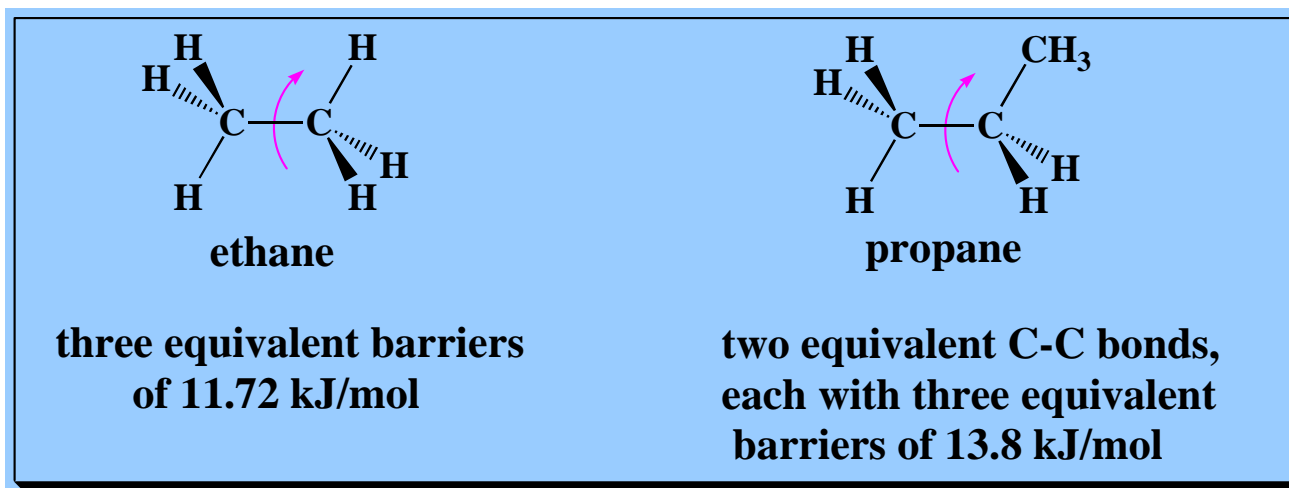


It is easier to see these conformational features by examining propane as a **substituted ethane** where a methyl group has replaced an H.



The barrier to rotation in propane is ~ 13.8 kJ/mol, slightly higher than the torsional barrier in ethane. Again there are three equal barriers in one complete rotation, each occurring at an eclipsed conformation. In propane, the eclipsing of a CH_3 group with an H does not significantly increase the barrier.

Summary of the Conformational Properties of Ethane and Propane

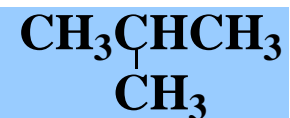


Conformational Features of the Butanes

There are two constitutional isomers of C_4H_{10} , butane and isobutane, with different conformational features.



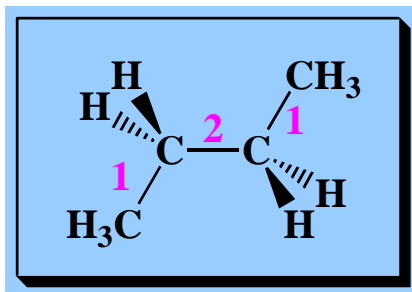
butane



isobutane

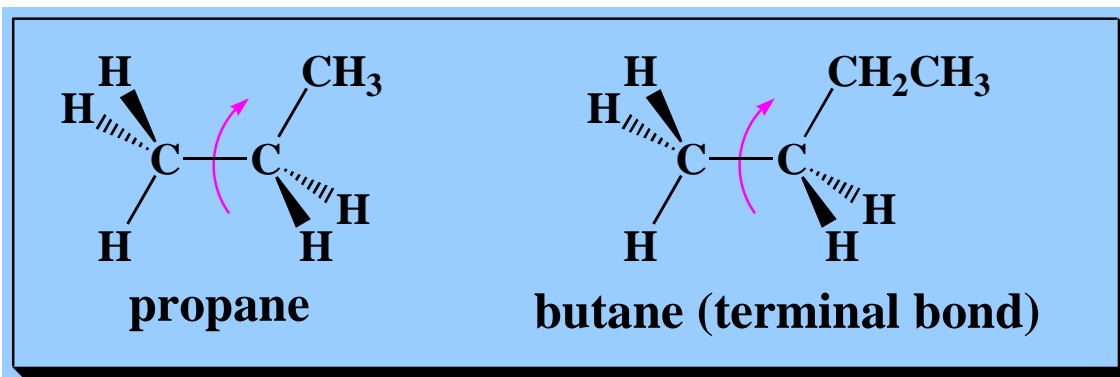
Butane

There are **two different C-C bonds** in butane, two "terminal" bonds (1) and one "internal" bond (2).



Conformational Features of the Terminal Bonds in Butane

The two equivalent terminal bonds in butane have the conformational features observed in propane, except that the energy barrier to rotation is slightly higher (15.1 kJ/mol compared with 13.8 kJ/mol).

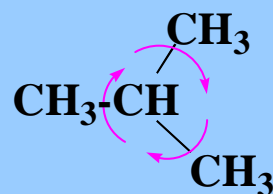


two equivalent C-C bonds,
each with three equivalent
barriers of **13.8 kJ/mol**

two equivalent terminal
C-C bonds, each with three
equivalent barriers of **15.1 kJ/mol**

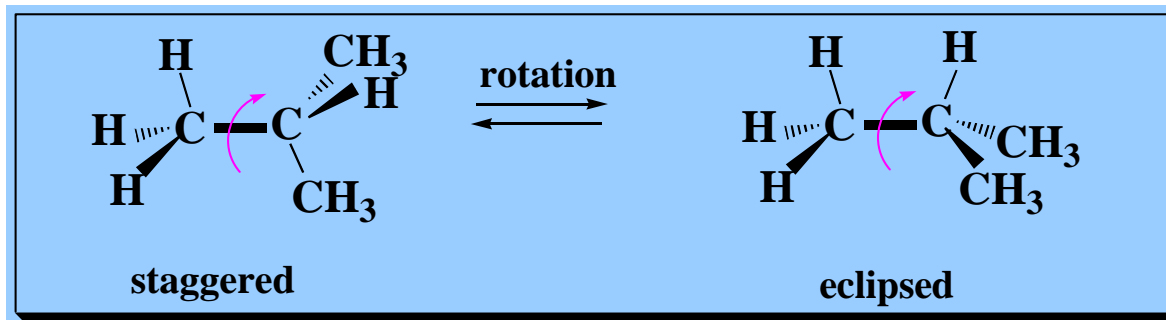
The Conformational Features of Isobutane

All three C-C bonds
in isobutane are
equivalent.



isobutane

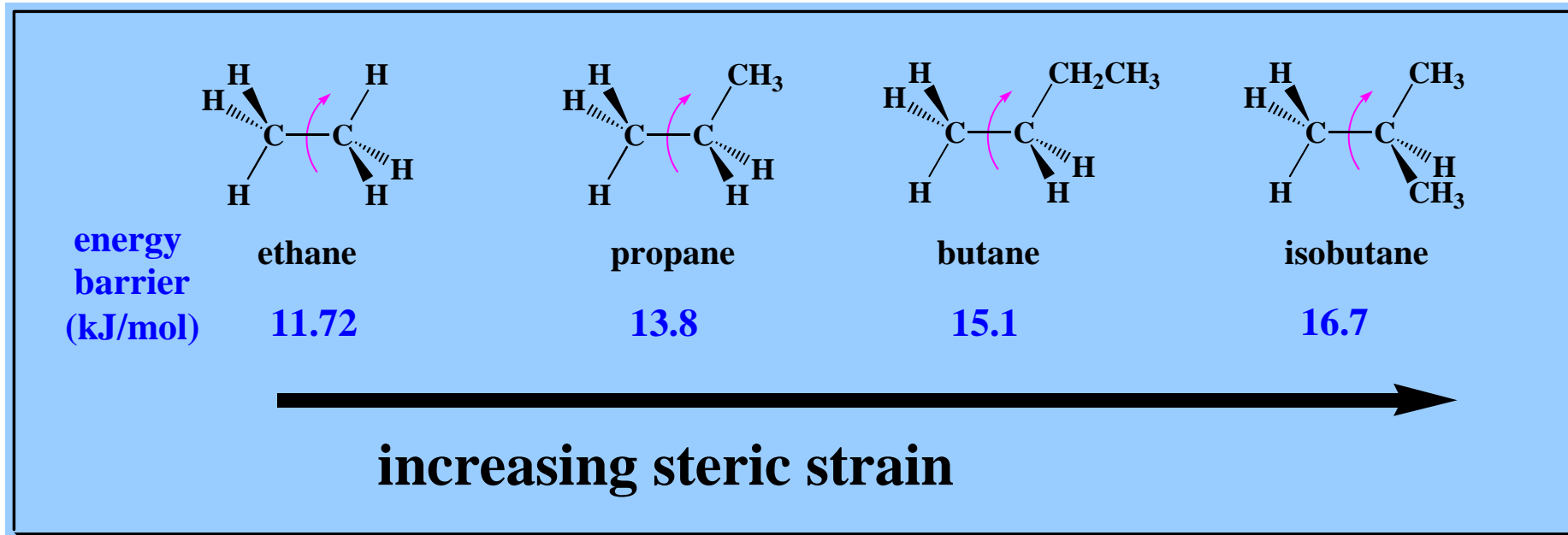
The conformational features may be more easily seen when isobutane is analyzed as a disubstituted ethane.



During a complete rotation around the C-C bond, there are **three equivalent staggered and three equivalent eclipsed conformations**. In the eclipsed conformation, there are **two alignments of CH₃~H** resulting in an energy barrier close to **16.7 kJ/mol**.

Overview of the Conformational Features of CH₃-CX₃ Systems

In a complete rotation around the C-C bond, there are **three equivalent energy barriers**. In simple ethane, the barrier is assigned to **torsional strain**. As CH₃ or other alkyl groups replace H, the barrier increases as elements of steric strain (nonbonded repulsive interactions) are introduced.



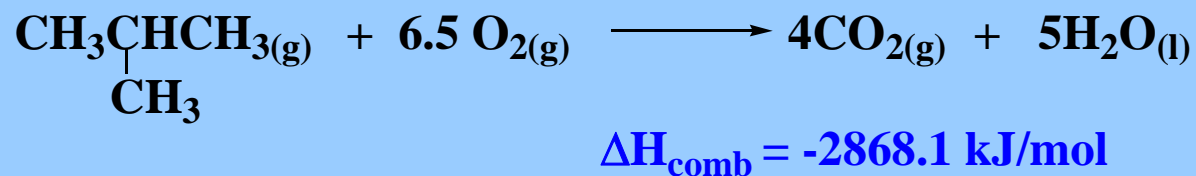
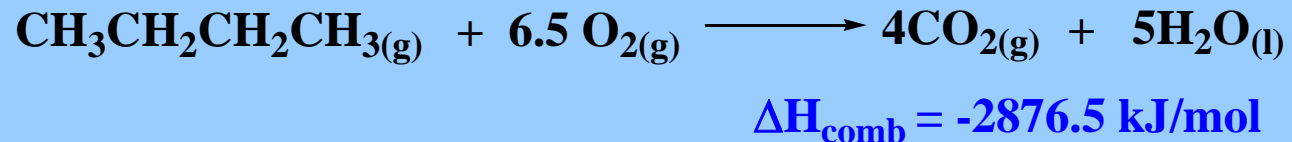
**Section 10--The Relative Stability of Cycloalkanes:
Ring Strain**

Stability of Isomers

The relative stability of **isomeric hydrocarbons** may be determined by measuring their heats of combustion under identical conditions.

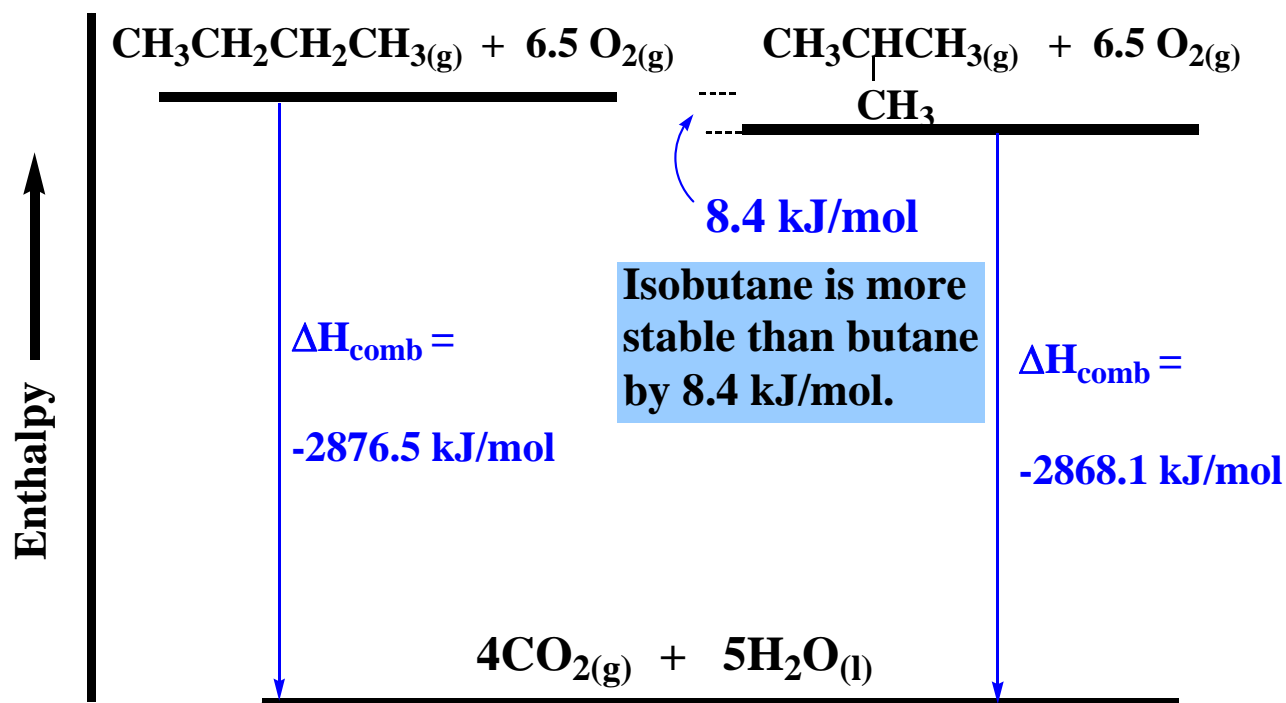
An Example: The Isomeric Butanes

The heats of combustion of the isomeric butanes are:



Analysis

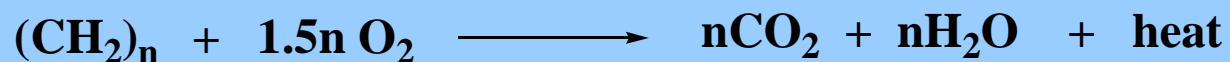
The analysis of the relative stabilities of the isomeric butanes from the above data is easiest to see in the energy state diagram below. Since the combustion reactions are **exothermic**, the product states are lower in energy than the reactant states. Since the **same product state** is produced in each combustion reaction, the levels of the two reactant states automatically are set by the amount of heat released. The difference in energy levels reflects the difference in energies of the isomeric butanes since O_2 is common to both reactant states.



Heats of Combustion of the Cycloalkanes: A Measure of their Relative Stabilities

The cycloalkanes form a homologous series $(\text{CH}_2)_n$ with $n \geq 3$.

The general reaction for the combustion of a cycloalkane is:



As n increases, more heat is evolved. In order to use the heats of combustion to determine the **relative stabilities** of the cycloalkane structures, the amount of heat evolved must be adjusted for the number of CH_2 groups. The table that follows provides this information.

Heats of Combustion of Cycloalkanes

cycloalkane (CH ₂) _n	n	ΔH_{comb} (kJ/mol)	heat evolved per CH ₂ group (kJ/mol)
cyclopropane	3	2091	697
cyclobutane	4	2744	686
cyclopentane	5	3320	664
cyclohexane	6	3952	659 ←
cycloheptane	7	4637	662
cyclooctane	8	5310	664
cyclononane	9	5981	664
cyclodecane	10	6636	664
unbranched alkanes			(659) ←

Note: The total amount of heat evolved increases with the size of the cycloalkane, as expected. However, the amount of heat evolved per CH₂ group is **highest for the smallest cycloalkanes**, and is lowest **for cyclohexane**, where the amount is consistent with that evolved in the combustion of unbranched alkanes.

Ring Strain in Cycloalkanes

Because the amount of heat evolved in the combustion of cyclohexane is consistent with the value expected from the combustion of unbranched (and unstrained) alkanes, it is assumed that **cyclohexane is free of any "strain energy."**

The greater amounts of heat evolved per CH₂ group in the other cycloalkanes are assumed to be due to elements of **"ring strain"** that lead to higher energies. The total amount of ring strain is calculated by multiplying **659 kJ/mol** x n, where n is the number of CH₂ groups, and subtracting this value from the measured heat of combustion.

Calculated Ring Strain in the Cycloalkanes

cycloalkane	n	ΔH_{comb} (kJ/mol) calculated	ΔH_{comb} (kJ/mol) measured	ring strain (kJ/mol)
cyclopropane	3	1976	2091	115
cyclobutane	4	2634	2744	110
cyclopentane	5	3293	3320	27
cyclohexane	6	3952	3952	0.0
cycloheptane	7	4610	4637	27
cyclooctane	8	5268	5310	42
cyclononane	9	5927	5981	54
cyclodecane	10	6586	6636	50

According to the above calculations, the greatest amount of strain energy is found in the very small cycloalkanes, **cyclopropane and cyclobutane**. Cyclohexane is "strain-free," and the larger cycloalkanes through cyclodecane have very small amounts of strain.

**Section 11--The Origin of Ring Strain in Cyclopropane and
Cyclobutane: Angle Strain and Torsional Strain**

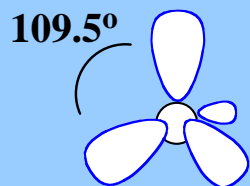
The Origin of Ring Strain in the Smaller Cycloalkanes: Angle Strain and Torsional Strain

The smaller cycloalkanes, cyclopropane and cyclobutane, evolve considerably more heat in combustion than expected for a hydrocarbon of their size. This difference, due to a higher energy content in these hydrocarbons, is called "**ring strain.**"

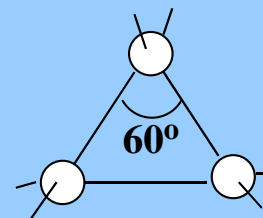
Angle Strain

One source of ring strain in the small cycloalkanes is "**angle strain,**" which is due to bonding factors.

The sp^3 hybridized carbon in an alkane projects the hybrid orbitals with a tetrahedral bond angle of 109.5° .



Cyclopropane has the geometry of a regular triangle with internal angles of 60° . The internal angle deviates from the idealized angle by 49.5° .



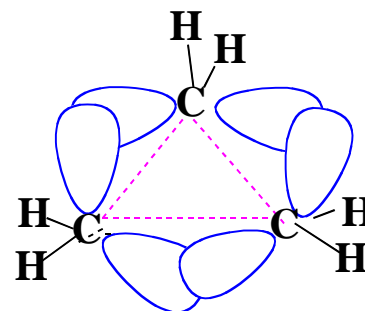
The compression of the internal internuclear angle in cyclopropane is called **angle strain.**

An Explanation of Angle Strain in Cyclopropane

One explanation of angle strain in cyclopropane is **poor orbital overlap**, sometimes referred to as "**bent bonds**."

The hybrid orbitals projected by the carbons in cyclopropane **are not along the internuclear axis** as required for maximum orbital overlap and stability.

The result is **weaker C-C bonds** (~272 kJ/mol compared with ~377 kJ/mol for a typical C-C bond), and higher relative potential energy for the cyclopropane structure.

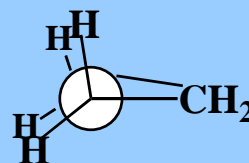
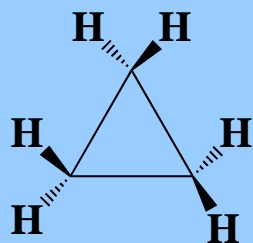


The C-C bonds in cyclopropane are often called "bent bonds."

The C-C internuclear distance is 1.510 Å, which is shorter than the 1.54 Å for the C-C bond in an alkane. The C-H bond length is 1.089 Å, shorter than the C-H bond in ethane (1.10 Å).

Torsional Strain in Cyclopropane

In addition to angle strain, there is **torsional strain** in cyclopropane because of the eclipsed hydrogens.



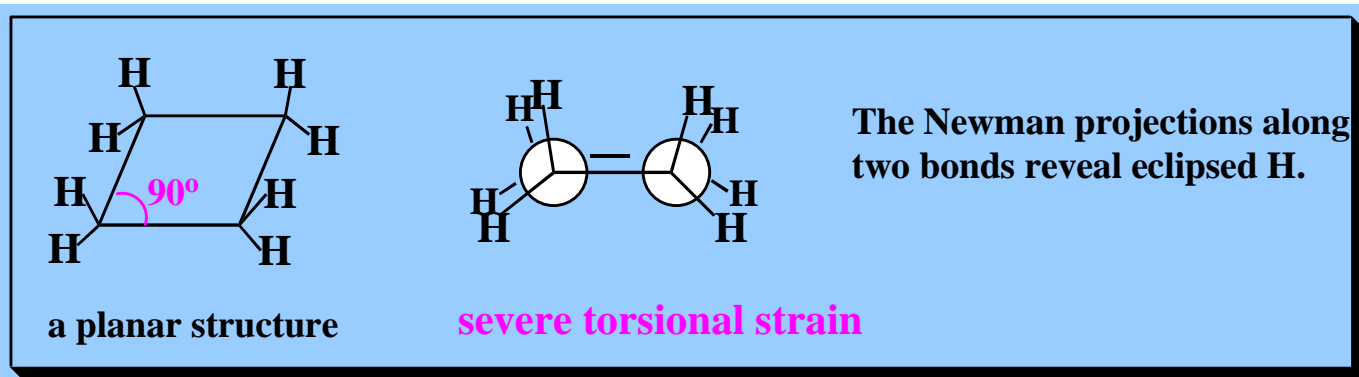
The Newman projection along a C-C bond reveals eclipsed H.

Because of the conformational rigidity of cyclopropane, the hydrogens are eclipsed along each C-C bond leading to severe torsional strain.

Cyclobutane

Cyclobutane also has both **angle strain and torsional strain**.

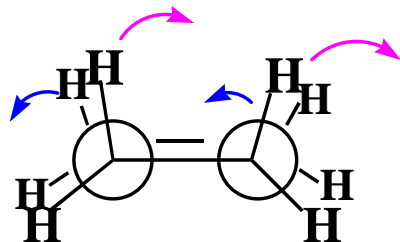
As in cyclopropane, the angle strain arises from the difference between the internal internuclear angle (close to 90°), and the idealized bond angle of 109.5° . If cyclobutane were planar, there would be severe torsional strain as well.



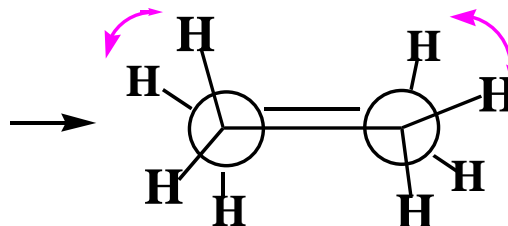
But, cyclobutane is not planar.

The Conformation of Cyclobutane

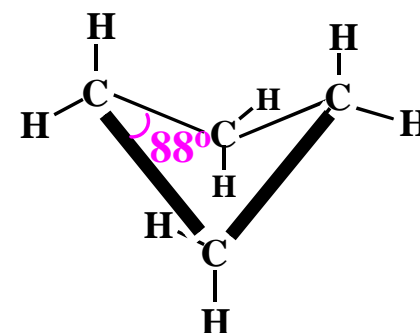
Cyclobutane has a **bent geometry**. This conformation is formed by a slight rotation around the C-C bonds. This rotation reduces the severe torsional strain in the planar geometry.



Clockwise and **counterclockwise** rotations around the C-C bond give the bent geometry.



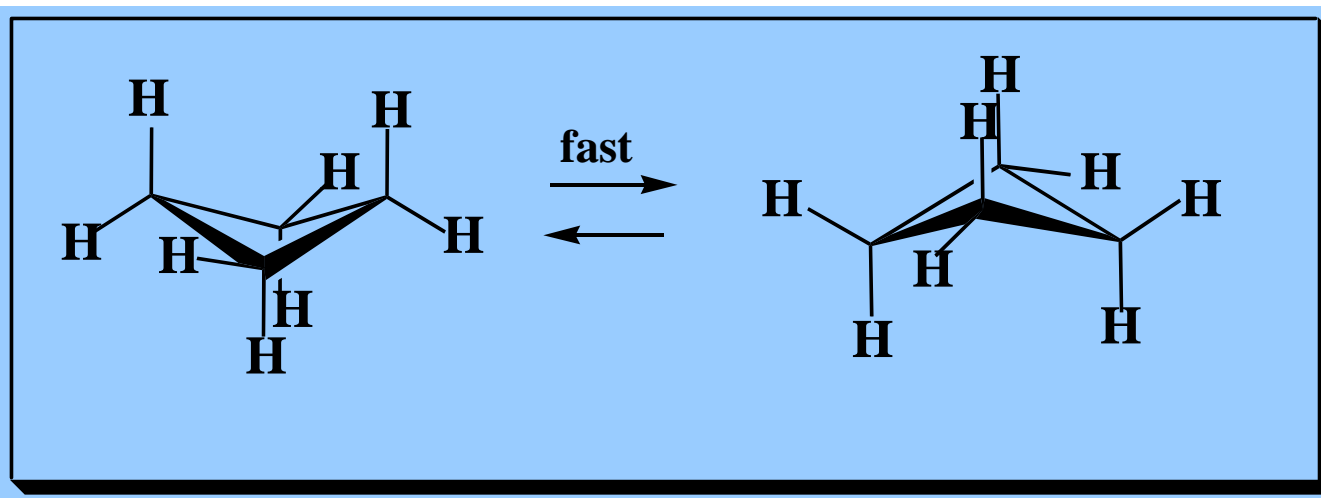
There is reduced torsional strain in the bent geometry.



There is a slight closing of the internal angle increasing angle strain in the bent structure.

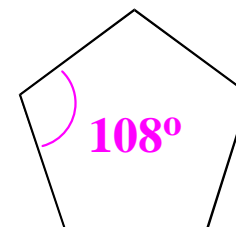
Inversion of the Bent Geometry

The bent cyclobutane structure **is not static**. The ring rapidly changes from one bent form to another with partial rotations around the C-C bonds.



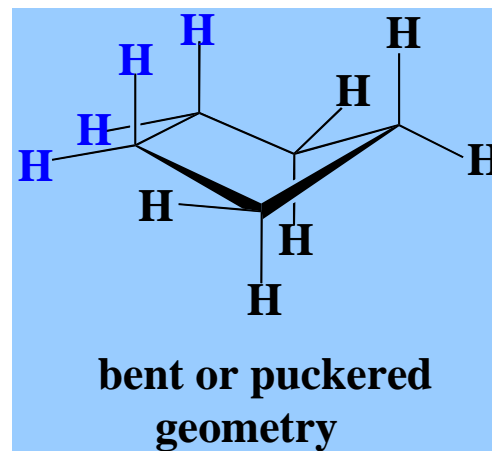
Cyclopentane

The internal angles of a regular pentagon are 108° , close to the idealized tetrahedral bond angles. Thus, a **planar cyclopentane** would have very little angle strain.



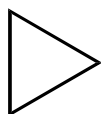
But a planar geometry would have **very severe torsional strain** (10 eclipsed H). Consequently, the geometry of cyclopentane is bent.

The torsional strain is reduced in the bent structure. **Four H** are still eclipsed, but 6 are staggered.



Quiz Chapter 4 Section 11

From an analysis of the heats of combustion of the following cycloalkanes, which ones contain elements of strain energy? From a conformational analysis, what are the significant types of strain energy in each cycloalkane?



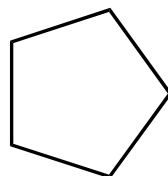
*significant
strain energy*

*torsional and
angle strain*



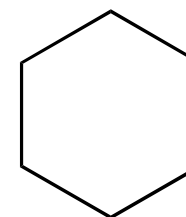
*significant
strain energy*

*torsional and
angle strain*



*small amount
of strain energy*

*torsional
strain energy*



*no strain
energy*

Section 12--Conformations of Cyclohexane

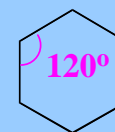
The Conformations of Cyclohexane

Baeyer Strain Theory

In 1885 Adolf von Baeyer (Univ. of Munich) proposed a theory to explain aspects of the chemistry of cycloalkanes. He assumed the structures were **planar**, and qualitatively estimated the amount of **strain** in each according to the difference between the internal angle of the regular polygon, and the idealized bond angle of the recently deduced tetrahedral carbon. This theory became known as the **Baeyer strain theory**.

Cyclohexane

Baeyer's theory predicts considerable strain in cyclohexane, which he assumed had the geometry of a hexagon with an internal angle of 120° .

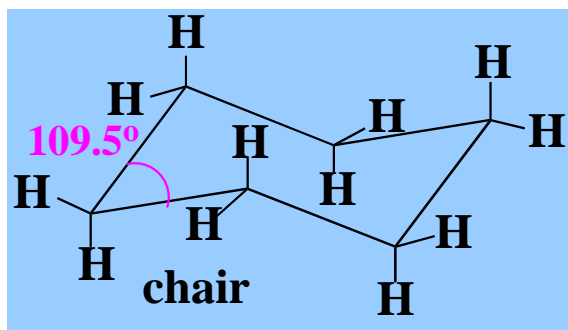


severe angle strain
in planar cyclohexane

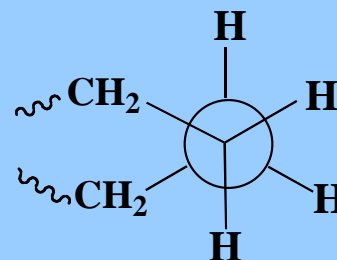
The prediction is **wrong** because cyclohexane is **not planar**. Cyclohexane exists in nonplanar geometries with the most stable being the "chair" with internal bond angles of 109.5° . In addition, there is no torsional strain in this conformation.

The Chair Conformation of Cyclohexane

The most stable conformation of cyclohexane is the chair in which there is **neither angle nor torsional strain**. The chair has the usual wig wag geometry of an alkane induced by linking a series of tetrahedral carbons.



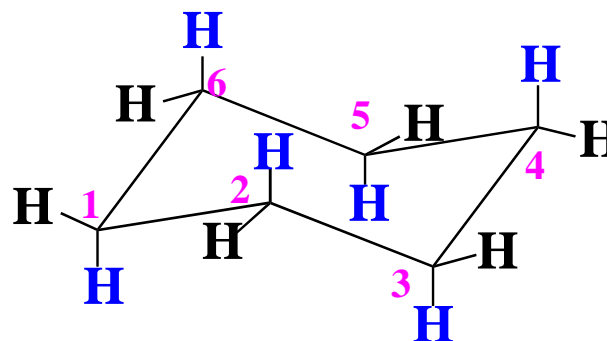
Newman
projection
view



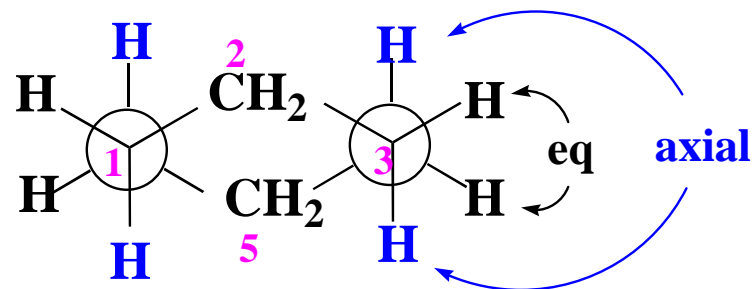
A Newman projection shows that the hydrogens are in a staggered conformation free of torsional strain.

Two Types of Hydrogens: Axial and Equatorial

There are two types of H in the chair conformation of cyclohexane: **6 axial (up and down)**, and 6 equatorial (close to the plane of the ring).

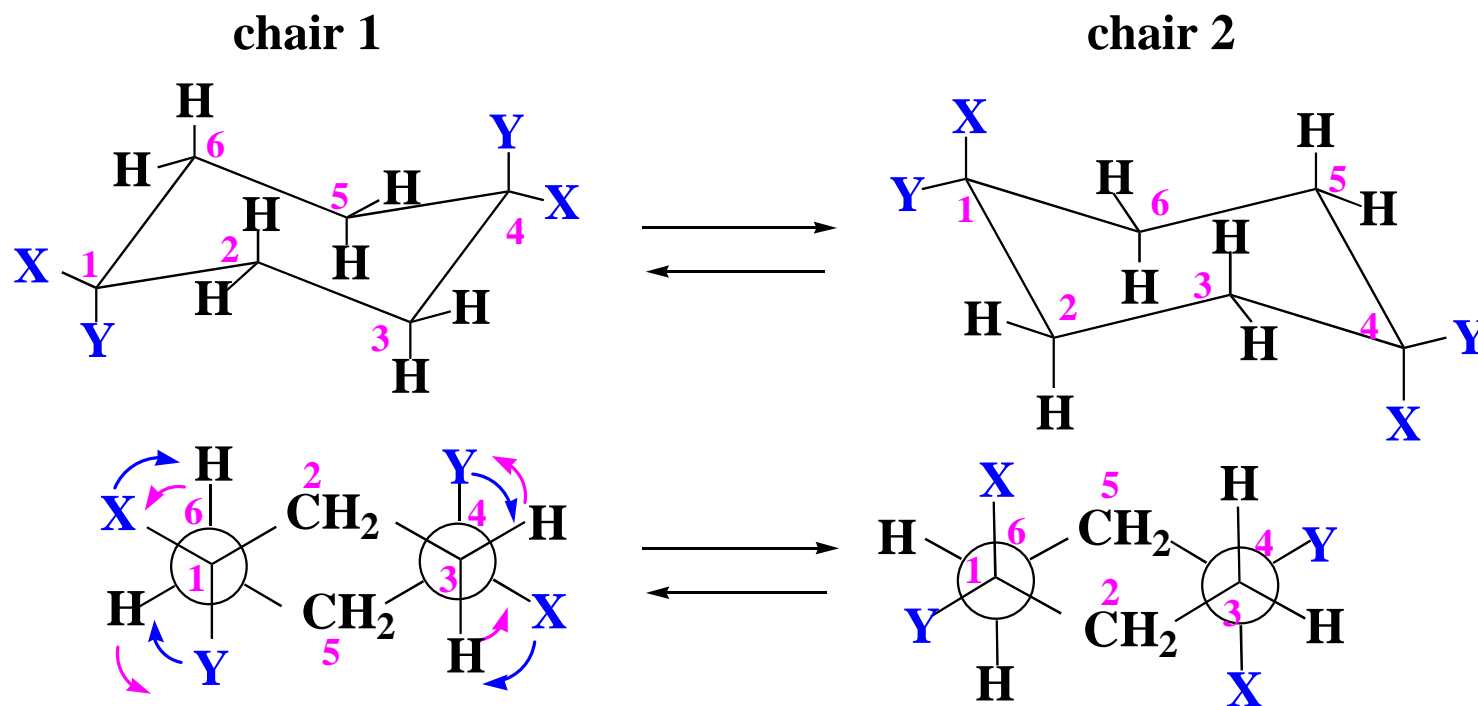


Newman projections along the C_1-C_6 and C_3-C_4 bonds show the different orientations of the **axial** and equatorial H.



Chair-Chair Interconversion

The chair conformation is not fixed. Partial rotations around C-C bonds lead to **chair to chair conversions**.



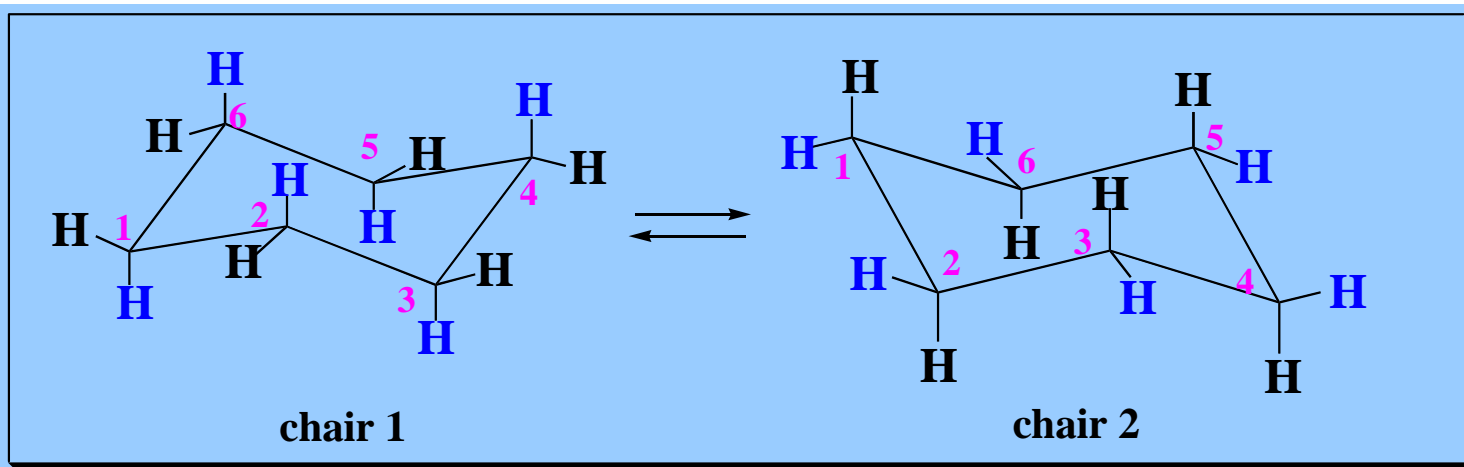
View chair 1 along the C₁-C₆ and the C₃-C₄ bonds for the Newman projection shown above.

In the Newman projection, imagine rotating carbons **1** and **4** **clockwise**, while rotating carbons **3** and **6** **counterclockwise**.

These rotations push carbon **2** down and carbon **5** up producing chair 2 and its Newman projection structure.

Axial-Equatorial Positional Exchange during Chair-Chair Interconversion

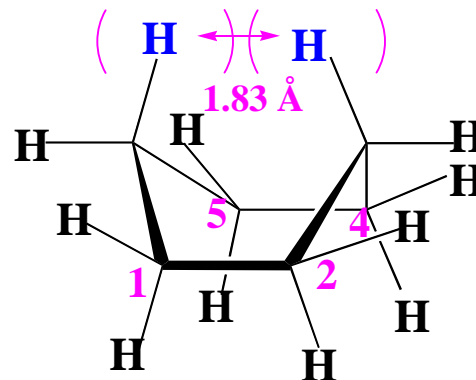
When one cyclohexane chair conformation transforms into the other chair conformation, the axial groups become equatorial groups and the equatorial groups become axial groups.



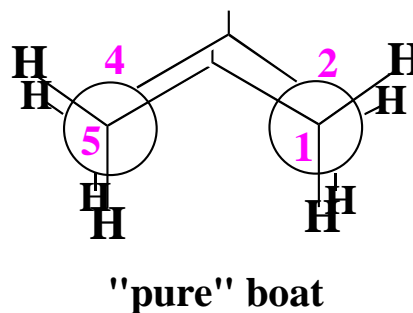
As will be discussed in detail later, there is a **fast equilibrium** between the two chair conformations of cyclohexane. If there are no substituents on cyclohexane, the two chairs are equivalent structures. But if one or more substituents are present, one of the chair conformations may dominate the equilibrium.

The Boat Conformation

Another conformation of cyclohexane that is free of angle strain is the **boat**.



The "pure" boat conformation (above) has **torsional strain** from eclipsed H as revealed by the Newman projections along the C_1-C_2 and C_5-C_4 bonds.



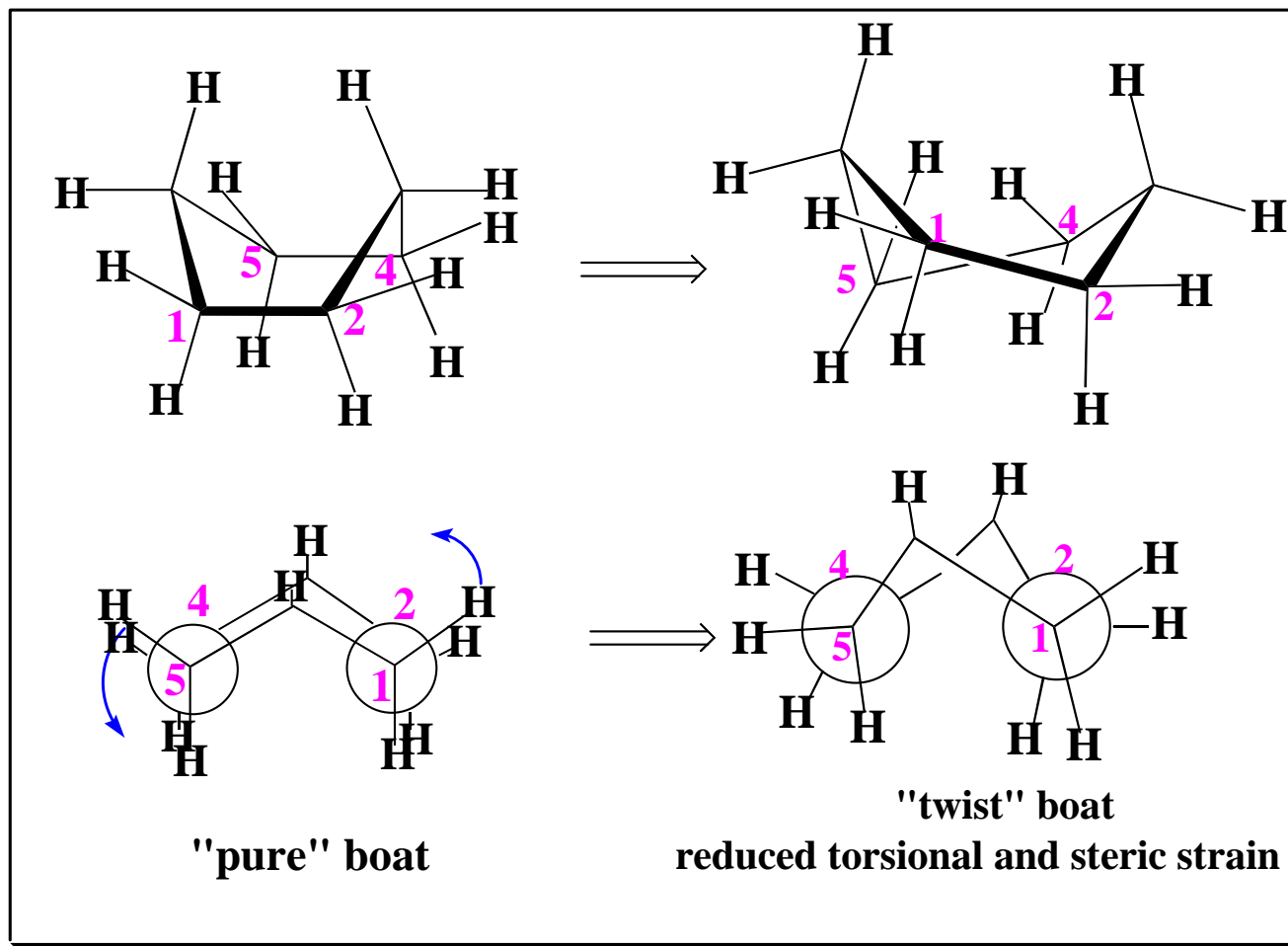
In addition, there is steric strain from nonbonded repulsive interaction between the two "flagpole" H that are closer than the 2.5 Å minimum distance apart for two H.

The Twist Boat Conformation

Because of torsional and steric strain, the "pure" boat conformation of cyclohexane is estimated to be **29.7 kJ/mol less stable** than the chair conformation.

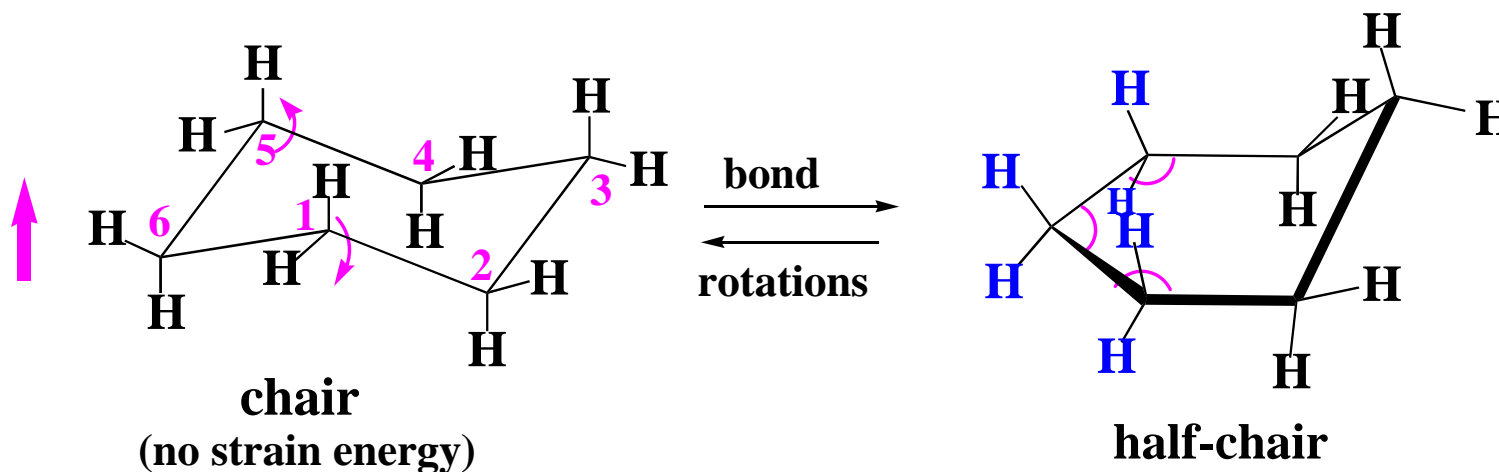
Some of the strain energy can be eliminated by a slight twisting (rotation) around the C_1-C_2 and C_5-C_4 bonds. The resulting conformation is called the "twist" boat.

The twist boat is less stable than the chair conformation by **23 kJ/mol**.



The Half-Chair Conformation

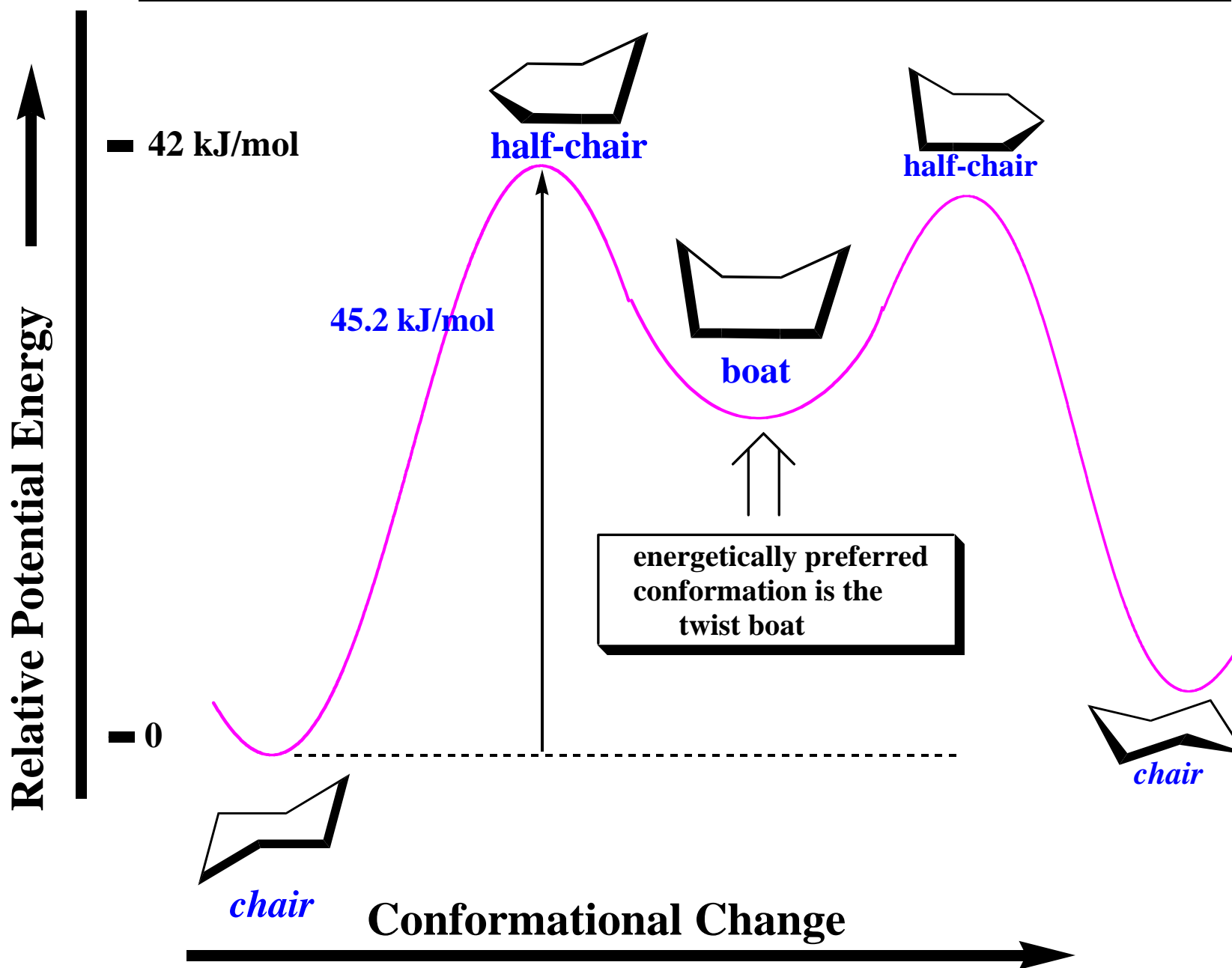
The half-chair conformation is not a stable conformation for cyclohexane. It actually is an **energy barrier (45.2 kJ/mol)** that must be overcome during the chair to chair conversion. An alternative path that passes through a completely planar cyclohexane would be considerably higher in energy.



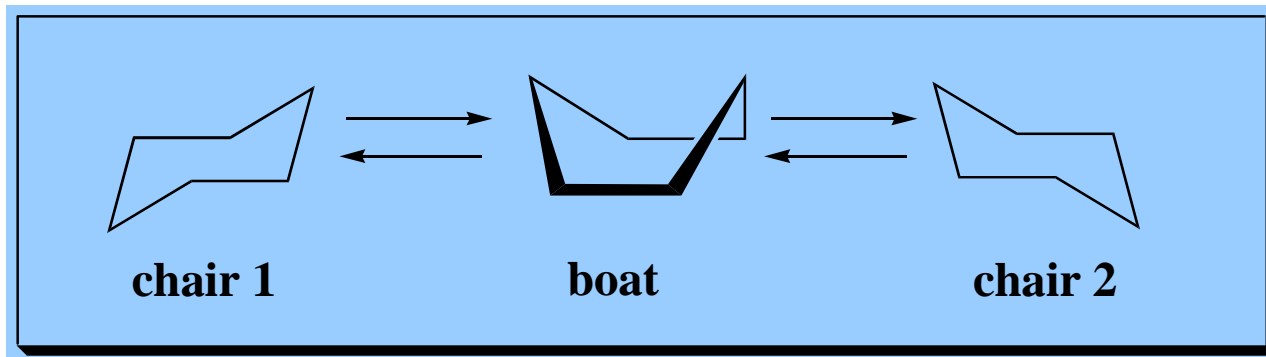
Partial rotations around the C_1-C_2 and C_4-C_5 bonds push C_6 into a plane containing C_1 , C_2 , C_4 , and C_5 .

The half-chair conformation has **angle strain** and **torsional strain** that place it 45.2 kJ/mol above the chair conformation.

Conformational Energy Diagram for Cyclohexane



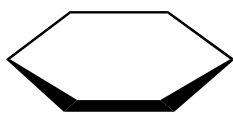
Some Key Observations



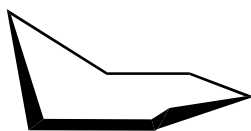
- (1) The energy barrier of 45.2 kJ/mol leads to a rate of **~10⁵** chair-chair interconversions per second at room temperature.
- (2) The difference in energy of 23 kJ/mol between the chair and twist-boat conformations means that, at room temperature, more than 99% of the cyclohexane molecules are in the more stable chair conformations. However, because of the rapid equilibrium, some cyclohexane molecules are always passing through the less stable twist-boat conformation.

Quiz Chapter 4 Section 12

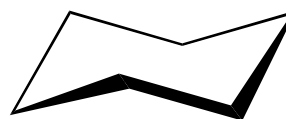
Name the following conformations of cyclohexane. Rank them in order from most to least stable. Indicate the type of strain energy present in each conformation.



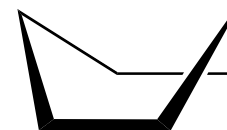
I



II



III



IV

Name:

planar

half-chair

chair

boat

Stability order (most to least): **III > IV > II > I**

Types of strain energy:

severe angle and torsional strain

angle and torsional strain

no torsional angle strain or steric strain

torsional and steric strain